

Reply to “Comment on ’Critique of the foundations of time-dependent density functional theory’ ”

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Abstract

In a recent Comment (arXiv:01710.0018), Maitra, Burke, and van Leeuwen (MBL) attempt to refute our criticism of the foundations of TDDFT (see Phys. Rev. A **75**, 022513 (2007)). However, their arguments miss the essence of our position. This is mainly due to an ambiguity concerning the meaning of the so-called mapping derivation of time-dependent Kohn-Sham equations. We distinguish two different conceptions, referred to as potential-functional based fixed-point iteration (PF-FPI) and direct Kohn-Sham potential (DKSP) scheme, respectively. We argue that the DKSP scheme, apparently adopted by MBL, is not a density-functional method at all. The PF-FPI concept, on the other hand, while legitimately predicated on the Runge-Gross mapping theorem, is invalid because the convergence of the fixed-point iteration is not assured.

Recently we have shown [1] that time-dependent density functional theory (TDDFT) is lacking a valid foundation. In a recent Comment (arXiv:0710.0018), Maitra, Burke, and van Leeuwen (henceforth referred to as MBL) claim to have found a fault in our argumentation. It seems, however, that due to an ambiguity concerning the so-called mapping derivation of the time-dependent Kohn-Sham equations MBL have failed to fully appreciate the essence of our objections to the TDDFT foundations. As a matter of fact, their reasoning can partly be seen as an unintended confirmation of our position rather than a refutation, as we will explain in the following.

Before addressing the central issue, let us rectify two minor misunderstandings brought up in the 2nd paragraph of the Comment, concerning the “apparent criticisms” of (i) the Runge-Gross (RG) action-integral functionals, and (ii) the use of non-local (external) potentials in DFT or TDDFT. The latter point, being the topic of Secs. 2 and 3 of our paper, is not at all meant as a critique of DFT (or TDDFT). On the contrary, this is a highly instructive confirmation of the logical consistency of DFT in view of an apparent contradiction. Second, we fully agree that the failure of the RG action-integral functionals [2] was recognized previously, as has been clearly stated in our paper (see Refs. 32 and 36). However, the breakdown of the original RG foundation of the time-dependent (TD) Kohn-Sham (KS) equations, assuming a stationarity principle for these functionals, is not widely known outside the inner TDDFT community. Therefore we have put particular emphasis on this point in our paper. Accepting this finding breaks the ground for the obvious question: How can TD KS equations be established without recourse to the RG action integrals?

To a certain extent the misconception of our arguments seems to be due to the fact that MBL do not always distinguish clearly between potential-functionals and potentials (as one should not confuse a function with the value of that function for a given argument). A potential-functional, such as the Kohn-Sham potential-functional (PF),

$$v_{KS} : \rho(\mathbf{r}, t) \rightarrow v_{KS}[\rho(t)](\mathbf{r}, t) \quad (1)$$

(referred to as $w[\rho(t)](\mathbf{r}, t)$ in our paper, see Eq. 75), is a prescription to construct a (time-dependent) potential $v(\mathbf{r}, t)$ for a given density, $\rho(\mathbf{r}, t)$. While the KS PF is trivial as a potential-functional, the specific potential

$$v_{KS}(\mathbf{r}, t) = v_{KS}[\rho_0(t)](\mathbf{r}, t) \quad (2)$$

associated with the exact TD density, $\rho_0(\mathbf{r}, t)$, of the interacting N -electron system under consideration is a highly non-trivial TD potential. Plugging it into the TD KS equation for a single orbital (assuming here the radical KS form),

$$i\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \{-\frac{1}{2}\nabla^2 + v_{KS}(\mathbf{r}, t)\}\psi(\mathbf{r}, t) \quad (3)$$

would allow one to determine the time-evolution of the exact one-particle density, $\rho_0(\mathbf{r}, t)$. However, the question is not if such a potential exists and, when available, could be used to solve the TD KS equation in the familiar way (that is by time-propagation). Indeed, the existence of $v_{KS}(\mathbf{r}, t)$ is almost a triviality, as was demonstrated in our paper for the rKS case. The actual problem is how to determine $v_{KS}(\mathbf{r}, t)$ (and thereby $\rho_0(\mathbf{r}, t)$) without making use of information obtained by somehow solving the full TD N -electron Schrödinger equation. Obviously, here the KS PF (1) is of no help. We have called it trivial, because it is completely unspecific (void of physical significance) and applies to any given TD density. The information necessary to generate the TD potential associated with a given TD density (trajectory), $\rho(t)$, has to be extracted from the density trajectory itself. To determine the respective potential at a given time t , $\rho(\mathbf{r}, t)$, $\dot{\rho}(\mathbf{r}, t)$, and $\ddot{\rho}(\mathbf{r}, t)$ are needed, as we have shown in Sec. 5 of our paper.

So what is the present foundation of TD KS equations, that is, as a density-based method to determine the density $\rho_0(t)$ of the specific interacting N -electron system? The procedure offered here is based on the first Runge-Gross (RG1) mapping theorem [2], establishing a fixed-point iteration scheme for the desired density $\rho_0(t)$. This derivation is completely analogous to the mapping foundation of the KS equations of static DFT, based only on the first Hohenberg-Kohn (HK1) theorem [3]. The TD KS approach essentially rests on the following three equations (adopting for simplicity the rKS formulation):

$$v_{KS}[\rho(t)](\mathbf{r}, t) \equiv v_{ext}[\rho(t)](\mathbf{r}, t) + J[\rho(t)](\mathbf{r}, t) + v_{xc}[\rho(t)](\mathbf{r}, t) \quad (4)$$

$$i\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \{-\frac{1}{2}\nabla^2 + u(\mathbf{r}, t) + J[\rho(t)](\mathbf{r}, t) + v_{xc}[\rho(t)](\mathbf{r}, t)\}\psi(\mathbf{r}, t) \quad (5)$$

$$\rho(\mathbf{r}, t) = N|\psi(\mathbf{r}, t)|^2 \quad (6)$$

The first equation (Eq. 81 in our paper) serves as a definition of the (non-trivial) xc potential-functional. Here $v_{ext}[\rho(t)](\mathbf{r}, t)$ is the potential-functional established by RG1 for

N interacting electrons. For a given TD density, $\rho(\mathbf{r}, t)$, this PF yields the TD potential recovering $\rho(\mathbf{r}, t)$ when used in the interacting N -electron TD Schrödinger equation. In particular,

$$v_{ext}[\rho_0(t)](\mathbf{r}, t) = u(\mathbf{r}, t) \quad (7)$$

where $u(\mathbf{r}, t)$ is the external potential of the system under consideration. In a similar way the (trivial) KS potential-functional, $v_{KS}[\rho(t)](\mathbf{r}, t)$, established by the RG1 mapping for the non-interacting KS system (or directly according to Eq. 75 of our paper), yields a potential that will recover $\rho(\mathbf{r}, t)$ when used in the TD KS equation. $J[\rho](\mathbf{r}, t)$ denotes the Hartree potential-functional.

By using the non-trivial xc PF in the KS equation (5) one obtains a fixed-point iteration scheme with the desired $\rho_0(\mathbf{r}, t)$ as fixed-point. This becomes particularly transparent by expressing $v_{xc}[\rho(t)]$ according to Eq. (4):

$$i\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \{-\frac{1}{2}\nabla^2 + v_{KS}[\rho(t)](\mathbf{r}, t) + u(\mathbf{r}, t) - v_{ext}[\rho(t)](\mathbf{r}, t)\}\psi(\mathbf{r}, t) \quad (8)$$

If (and only if) $\rho(\mathbf{r}, t) \equiv \rho_0(\mathbf{r}, t)$, the two latter potentials on the r.h.s. cancel each other, and the KS equation with the remaining potential $v_{KS}[\rho_0(t)](\mathbf{r}, t) = v_{KS}(\mathbf{r}, t)$ will yield the fixed-point density $\rho_0(\mathbf{r}, t)$.

However, as it stands, this is just an *ad hoc* fixed-point iteration scheme. To qualify as a method for determining $\rho_0(\mathbf{r}, t)$ the question of convergence must be settled, at least in principle. But so far there is no proof of the possibility of convergence. So even if one had the exact xc PF, $v_{xc}[\rho(t)]$, this would be of no avail to determine the fixed-point solution, because one cannot expect the fixed-point iteration (referred to as trajectory mode solution in our paper) to converge. The situation here is completely different from the case of static DFT, where the fixed-point iteration is the standard method to determine the ground-state density $\rho_0(\mathbf{r})$. In static DFT, by contrast, the variational principle according to the second Hohenberg-Kohn theorem (HK2) assures the convergence of the fixed-point iteration as a means of finding the (existing) minimum of the energy functional.

In the TDDFT community, the lack of a proof of convergence for the TD KS fixed-point iteration has never been seen as a problem. To the best of our knowledge, the problem has not even been mentioned in the TDDFT literature. There was no reason to worry about the fixed-point iteration at all, because there was an apparent silver bullet: direct time-propagation of the TD KS equation (5). By starting from the exact static ground-state

density, $\rho_0(\mathbf{r})$, at the onset of the TD interaction, say at $t = 0$, it was believed that one could propagate the initial KS orbital through a given time by supplying the required density argument in $v_{xc}[\rho(t)](\mathbf{r}, t)$ (and $J[\rho(t)](\mathbf{r}, t)$) “on the fly” via Eq. (6). While this would work for instantaneous potential-functionals (as those used in the adiabatic approximation), the potential-functionals in general cannot be expected to be instantaneous. As we have explicitly shown in our paper, the KS potential-functional $v_{KS}[\rho(t)](\mathbf{r}, t)$ required in the definition (4) of $v_{xc}[\rho(t)](\mathbf{r}, t)$ depends on the second time-derivative of the density, which undermines the possibility of propagation. The eventuality that the potential-functionals used in the TD KS equations are non-instantaneous in the described sense has never been seen and addressed before. The inescapable conclusion of that finding is that the TD KS equations as established by the RG1 mapping theorem do not represent physical equations-of-motion, which could be treated by time-propagation. The silver bullet is an illusion.

Let us emphasize once again: the dependence on the second time-derivative of the density trajectory (and thus on the infinitesimal “past” and “future” of the density at a given time t) pertains to the potential-functionals, $v_{KS}[\rho(t)]$, and $v_{xc}[\rho(t)]$. We do *not* claim that this finding applies to the KS potential, $v_{KS}(\mathbf{r}, t)$, itself, as MBL erroneously assume. As a matter of fact, $v_{KS}(\mathbf{r}, t)$ can be determined directly, but only by somehow solving the full TD Schrödinger equation (FTDSE) for the original N -electron system. We do not at all deny that such a direct FTDSE based determination of $v_{KS}(\mathbf{r}, t)$ can do perfectly well without second time-derivatives of the wave function or the density. Most of the Comment by MBL is devoted to demonstrate just that.

As was pointed out in our paper, the rKS formulation allows for an obvious direct approach to $v_{KS}(\mathbf{r}, t)$ by solving the FTDSE (e.g. by propagation starting at $t = 0$), thus yielding the exact TD density, $\rho_0(\mathbf{r}, t)$, which in turn can be inserted as argument in the explicitly available (trivial) KS potential-functional, $v_{KS}(\mathbf{r}, t) = v_{KS}[\rho_0(t)](\mathbf{r}, t)$. (This way to determine $v_{KS}(\mathbf{r}, t)$ from $\rho_0(\mathbf{r}, t)$ is also referred to as the inversion of the TD KS equation.) In the final inversion step, being based only on the density information and a potential-functional, the 2nd time-derivative of the density is required, which, of course, causes no problem here, as the density trajectory is available anyway, along with its first and second time-derivatives.

At this point MBL think they have refuted us, namely, by demonstrating that a direct (FTDSE based) determination of $v_{KS}(\mathbf{r}, t)$ is possible without recourse to second derivatives,

that is, depending only on the past. But this misses our point completely. The requirements of a direct (FTDSE based) approach to $v_{KS}(\mathbf{r}, t)$ are completely irrelevant to our criticism of the validity of predictive TD KS equations according to Eqs. (4 - 6). The real issue are the properties of the involved potential-functionals: What is actually needed to generate a potential at a time t via a potential-functional? As we have shown explicitly: the density at t , together with its first and second time-derivative at that time.

Here we are closing in to the core of the controversy. Apparently, MBL see the essence of TDDFT in Eq. (3) together with the possibility to determine the KS potential, $v_{KS}(\mathbf{r}, t)$, in a direct way. But it should be clear that such a direct approach to $v_{KS}(\mathbf{r}, t)$ is, perhaps, an interesting detour to determine $\rho_0(\mathbf{r}, t)$ by ultimately solving the full TD Schrödinger equation, but certainly not a density-functional method. Unfortunately, the distinction between the latter direct KS potential scheme and the genuine density-functional approach (Eqs. 4 - 6) is rather blurred than clarified in the TDDFT literature. Astonishingly, there is no such thing as a second founding paper (of the theorem-proof type), filling the void after the breakdown of the original RG foundation. Even more disconcerting is the instance that the PF-FPI procedure, while well-known in the inner TDDFT community, has not been presented in the literature so far. What is offered instead (see, for example, the review article by Marquardt and Gross [4]) is rather misleading. It is insinuated that a non-trivial xc PF can be obtained by just subtracting the Hartree PF and the given external potential, $u(\mathbf{r}, t)$, from the trivial KS PF. While the TD KS equations then assume the familiar, reassuring shape of physical equations-of-motion, apparently amenable to time-propagation after making a good guess for the xc PF, the real issue of establishing a density-based method for td systems has got out of sight.

Finally let us take a look at the specific derivations presented in the Comment. Here MBL demonstrate the possibility to construct the exact xc potential, $v_{HXC}(\mathbf{r}, t)$ in their notation, directly without recourse to second time-derivatives of the TD density. But as can readily be seen, this direct approach is predicated on solving the FTDSE. Here the key is to note that the Sturm-Liouville type Eq. C(3) of the Comment, underlying the construction of $v_{HXC}(\mathbf{r}, t)$, depends explicitly on the quantity (Eq. C2)

$$q(\mathbf{r}, t) = \langle \Psi(t) | \hat{q}(\mathbf{r}) | \Psi(t) \rangle$$

that is, an expectation value involving the the N -electron TD wave function $\Psi(t)$. This

makes apparent that the construction of the xc potential at a given time t along Eqs. C(1) to C(4) depends on the TD (N -electron) wave function, $\Psi(t)$ at t .

Since according to Eq. C(3) $v_{HXC}(\mathbf{r}, t)$ (at a given time t) is completely determined by $\Psi(t)$ (and by the density $n(t)$, being itself determined by $\Psi(t)$), one can readily devise a time-propagation scheme for $v_{HXC}(\mathbf{r}, t)$ based on time-propagation of $\Psi(t)$. The time-propagation of $v_{HXC}(\mathbf{r}, t)$ can, in turn, be used in the propagation of TD KS equations. Like the original time-propagation of $\Psi(t)$, the (simultaneous) time-propagations of $v_{HXC}(\mathbf{r}, t)$ and the TD KS equations are viable procedures, depending only on the previous (past) time steps. The actual route taken in the demonstration along Eqs. C(5-11) is slightly different, though. Rather than using time-propagation for $\Psi(t)$, the procedure adopted by MBL amounts to expanding $\Psi(t)$ in terms of a Taylor series at $t = 0$. The first step, spelled out in Eq. C(8), establishes $\partial_t \Psi(\Delta t) = -i\hat{H}(0)\Psi(0)$, which readily leads to the commutator expression on the rhs of Eq. C(8). In the general (k th) time step, $q(\mathbf{r}, t)$ can be written in a form involving multiple commutators of $\hat{q}(\mathbf{r})$ and $\hat{H}(0)$ sandwiched by $|\Psi_0\rangle = |\Psi(0)\rangle$ (see text after Eq. C11). Obviously, the multiple commutators arise from terms of the kind $\hat{H}(0)^n|\Psi_0\rangle$ with increasingly higher powers of $\hat{H}(0)$.

Let us note that the Taylor-type expansion of $\Psi(t)$ means a severe restriction with respect to genuine time-propagation. The Taylor representation (at $t = 0$) is valid only for a time-independent Hamiltonian and, moreover, presupposes that the wave function is analytic in time at $t = 0$. (Already the 2nd time derivative of the wave function is discontinuous at $t = 0$ for a simple TD potential of the form $\sim \Theta(t)t$.)

In any case, what MBL have shown here is that the exact xc potential can be constructed directly and used in a viable time-propagation scheme of the TD KS equations - if the N -electron wave-function $\Psi(t)$ is at the disposal. As explained above, we have no objections against this demonstration, it just misses the point.

As our Reply has grown somewhat long, it may be helpful to summarize the essentials. 1) After the breakdown of the original foundation of TDDFT based on the RG action-integral functionals and their stationarity principles, there is a confusion about the essence of the alternative mapping derivation of TD KS equations, resting on the RG1 mapping theorem. The authors of the Comment seem to adhere to an idea denoted as direct KS potential (DKSP) scheme here. By contrast, there is a more common view that the TD KS equations have to be established as a fixed-point iteration scheme for potential-functionals (PF-FPI),

following here an analogous approach in static DFT. 2) In our paper we have shown that the PF-FPI concept is not valid because, by contrast to static DFT, the convergence of the fixed-point iteration is not assured. The apparent way out, that is, time-propagation of the TD KS equations (in the PF-FPI notion) fails because the potential-functionals require the second time-derivative of their density arguments. Our criticism of the PF-FPI concept has not been addressed, let alone refuted by MBL, focussing rather on the DKSP scheme. 3) We argue that the DKSP scheme is not a density-functional method at all (i.e. based entirely on densities and density potential-functionals), because there is no way to determine the required KS potential, $v_{KS}(\mathbf{r}, t)$, other than by somehow solving (or approximating) the full (interacting N -electron) TD Schrödinger equation. As an unintended confirmation of this point one may see the large passage in the Comment where MBL show that the DKSP equation can be propagated without the need for second-time derivatives: unwittingly they here make use of the time-propagation of the full N -electron wave function.

In conclusion, the status of TDDFT as an in principle rigorous approach to the time-evolution of an interacting many-electron system, must still be considered as completely unfounded. Instead of advocating “many more exciting real-life applications” of TDDFT, a major effort should be made to ultimately clarify the question whether one can derive predictive equations-of-motion formulated entirely in terms of densities, that is, without recourse to the wealth of phase information guiding the time-evolution of the many-electron wave functions. It is highly questionable if one will be able to derive density-based physical equations-of-motion at all, but it will be next to impossible to do so without a valid variational (or stationary) principle.

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